PERGAN
The Peroxide Company

Technical Bulletin

# Curing unsaturated polyester-, vinylester- and acrylate resins

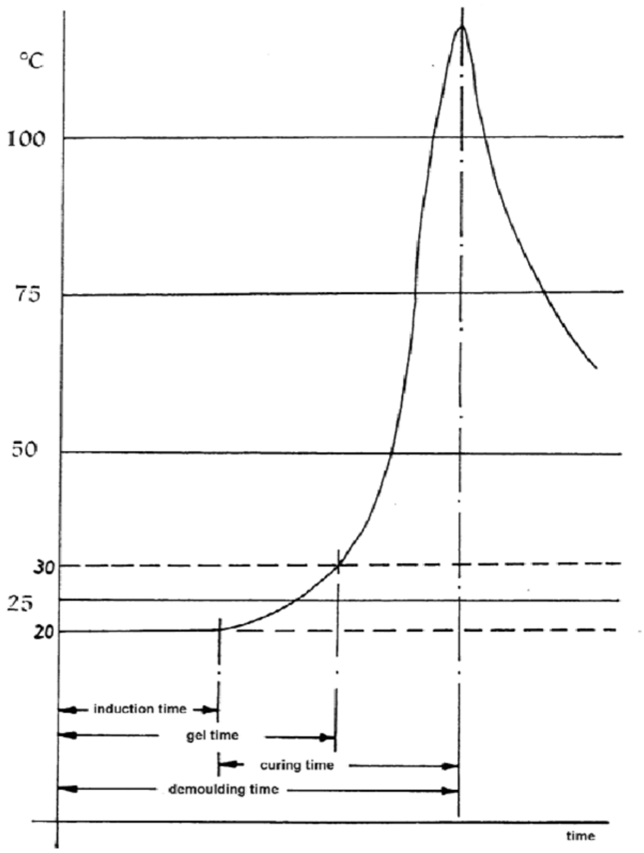
## with Organic Peroxides, accelerators and other additives

## Introduction

This technical bulletin deals with the use of organic peroxides for curing of unsaturated polyester resins and vinylester resins. It should give the reader a rough insight on the function of this process and the available peroxides that can be used.

## General Information on Curing of Unsaturated Polyester Resins (UP resins)

The processing of UP resins, especially glassfiber reinforced UP resins, has become very important over the last 50 years. The main reasons for this are that processing of UP resins requires just simple manual procedures without any expensive investments.
Unsaturated Polyesters are formed by polycondensation reaction of alcohols (like Glycols and Bisphenoles) and dicarboxylic acids (unsaturated dicarboxylic acids, e.g. maleic acid or fumaric acid, as well as saturated dicarboxylic acids, e.g. orthophtalic acid or isophtalic acid). Properties of the final cured UP resin can be influenced by variation of the raw materials, utilized for the unsaturated polyester (e.g. toughness, chemical resistance, strength, reactivity, degree of crosslinking). The unsaturated polyesters are mixed with unsaturated monomers, e.g. styrene, yielding the UP resin. The styrene content of common UP resins is 30 % - 40 %. A too high Styrene content will lead to a decrease of strength in the cured final part.
UP resins are cured with free radicals, resulting from decomposition of organic peroxides. The prganic peroxides decompose either by the influence of heat (so called Hot Curing) or by the influence of appropriate accelerators (so called Cold Curing). The unsaturated polyester molecules polymerize with the styrene resulting in a three dimensional though network (so called duromer or thermosetting material)




The curing reaction of the activated resin (that means UP resin + peroxide + accelerator) can firstly be detected by a transition of the more or less viscous liquid to a soft solid, the gel. Before gelation starts, the activated resin can be processed, therefore the period of time before gelation starts is called the manufacturing time or pot life. During the further solidification of the resin the heat of polymerization is dissipated, resulting in an increase of temperature up to a certain maximum level (peak temperature). Throughout the following cooling a reasonable volume shrinkage of the cured part can be obtained.
The material properties (e.g. thermal and chemical resistance) of a cured part made from high quality UP resin depend on the degree of crosslinking. A low degree of crosslinking results in not sufficient material properties. The degree of crosslinking of a cured UP resin depends on the curing system (organic peroxide / accelerator), the curing time, the curing temperature and - if required - the post curing conditions.

## Criterions for Selection of an appropriate Curing System

In order to find the best solution, the following has to be taken into consideration:

- Processing conditions
- Shape and size of final cured parts
- Type of resin, fillers and other additives required

### Processing Conditions

The processing conditions are mainly depending on the selected working process. The following working processes are common:

- Hand Lay-out
  This means to put by hand glass fiber mats in an open mould and to soak them with the activated resin. A more automatic version is to spray a mixture of fiber, resin, hardener and accelerator onto the mould (the resin, hardener and accelerator are dosed separately and mixed within the spray gun with the fibers). Big final parts can produced with this working process, which is designed only for cold curing systems.

- Rotational Moulding of  big parts
  In a rotating mould (a hollow cylinder) a mixture of roving fibers and activated resin is dosed by use of a lance. Due to the rotation the mixture of fibers / resin is spread homogeneously on the inner surface of the mould. With this working process tubes, silos and tanks can be produced with an excellent inner and outer surface quality. This methode is also designed for cold curing systems.

- Filament Winding
  On a cylindrical, rotating mould rovings are winded like a spiral. Either the rovings are soaked with the activated resin before winding or after they have been winded onto the mould. Cylindrical and spherical hollow parts (tubes, silos or tanks) can be produced with this method, which is only designed for cold curing systems.

- Pultrusion
  A continuous method, where rovings are first pulled through a bath of activated resin and then pulled through a heated mould. With this method, which is only designed for hot curing systems, rods and hollow profiles of variable thickness can be produced.

- Pressing
  In a mould glass fiber mats and an appropriate amount of activated resin is filled. Closing of the mould will result in a homogeneous distribution of the resin. This method is suitable for cold as well as for hot curing systems.

- SMC / BMC
  SMC (Sheet moulding compounds):
  Roving fibers are soaked with the activated resin. Processing by rolls will yield in long sheets of resin mats which are coiled afterwards and stored (for thickening / ripening).
  BMC (Bulk moulding compounds):
  Short roving fibers are soaked with the activated resin and stored for ripening.
  Working process for SMC is pressing, for BMC pressing or injection moulding. Curing of SMC / BMC is only be performed by hot curing systems.

- Casting / Rotational Moulding
  The activated resin (with or without filler) will be filled in cast moulds or is rotated in cylindrical forms. Final parts made from resin with high filler content are e.g. tubes from polymer concrete or plates with marble as fillers. Parts made from resin without filler are for example buttons.
  Cold curing and also hot curing systems can be applied.

- Coating
  This means repair of car bodies, artificial stone plates and floors. This is performed by utilizing pre-accelerated putties. Also the hardener is utilized in paste form. It is a cold curing system, a post curing is not usual.

After having selected the working process the following questions arise:

- How many final parts have to be produced during a certain period of time? Is an expensive machinery necessary, which can only produce economically at a high production rate and short cycle time?

- Is the selected working process suitable for cold and / or for hot curing systems? Is it a continuous or discontinuous process? Will be operated in closed moulds or non closed moulds, under the influence of ambient air (inhibition of free radicals)?

- What is the requirement concerning pot life of the activated resin (hours, days, weeks)? Is it possible to operate with separated dosage of hardener and accelerator?

These questions will result in a requirement profile of the curing system, i.e. the decision on utilization of a cold, resp. hot curing system, the required pot life of the activated resin, the curing time and - related to this - the curing temperature as well as a potentially necessary post curing.

### Shape and Size of the Final Cured Parts

These parameters - or more important - the thickness of the final parts are also important criterions for the selection of the best suitable curing system. Two extreme examples may underline this:

- In very thick parts the heat of polymerization cannot be sufficiently dissipated. As a result one can obtain peak temperatures up to 250 °C, which is, in combination with the volume shrinkage during cooling, leading to stress cracks. These can be avoided by utilization of a special curing system which allows a dissipation of the heat of polymerization over a longer period of time, resulting in lower peak temperatures.

- During curing of thin layers (e.g. gelcoats) no increase in temperatures may be detected, as the generated heat is completely dissipated to the ambient surrounding, resulting in an insufficient degree of curing. Choosing a high reactive curing system with a high exothermic behavior will solve this problem.

However, in laminates with various wall thicknesses in one part both extremes (maybe not to the extent described above) may occur.

### Types of Resins, Fillers and other Additives required

Normally all common types of resins, fillers and additives (pigments and / or lubricants) are approved to be suitable for curing with peroxide based systems. However, certain mineral fillers may absorb accelerators and therefore inactivate them. Some pigments may catalyze the decomposition of the peroxides. This may require the replacement of the selected curing system by a special peroxide / accelerator system, which is not sensitive to the above described.

## Cold Curing / Hot Curing (Curing systems with and without accelerators)

At temperatures below approx. 80 °C inside the part to be cured, peroxides have to be utilized in combination with appropriate accelerators, in order to accelerate the peroxide decomposition. A characteristic of the so-called "Cold Curing" is therefore not only the lower processing temperature, but the utilization of accelerators.

Curing without addition of accelerators requires temperatures within the parts to be cured from approx. > 80 °C. Typical temperatures of the so called "Hot curing" process are 120 °C up to 160 °C. These temperatures are necessary to achieve a reasonable degree of curing within a short time. At a certain temperature level the use of accelerators are without effect or may even negatively influence the curing process.
It is not necessary to discuss advantages / disadvantages of cold / hot curing systems, as the criterions mentioned in the previous chapter already anticipate the decision for a cold or hot curing system. However, for all cold curing systems it can be stated that a complete cure without post curing or assisting the curing process with external heat will not lead to an optimal degree of cure.

### Cold Curing Systems

In practice two different systems are in use:

- Amine accelerated cold curing systems (with Dibenzoyl peroxid as hardener)
- Cobalt accelerated cold curing systems (with Ketone peroxides, like Methyl Ethyl Ketone peroxides or Acetylacetone peroxides or Cyclohexanone peroxides as hardener).

The following table shows an overview of the advantages / disadvantages of both systems:

| System | Advantages | Disadvantages |
|---|---|---|
| **Amin Accelerated Cold Curing** | • long potlife<br>• fast curing, also below ambient temperatures<br>• not very sensitive with respect to humidity | • yellowing<br>• post curing required<br>• final degree of curing lower with respect to Cobalt accelerated cold curing |
| **Cobalt Accelerated Cold Curing** | • bright colour of cured parts<br>• slow curing<br>• final parts have no tendency for stress cracks | • long demoulding time<br>• post curing required |

## Amine Accelerated Cold Curing Systems

These cold curing systems are working with tert.-Alkyl Amines in combination with Dibenzoyl peroxide. The following Dibenzoyl peroxide formulations are part of our product range.

| Physical Form: | Name: | Remarks: |
|---|---|---|
| | PEROXAN BP-Powder 50 W | 50 %, filler: solid Phthalate |
| | PEROXAN BP-Powder 50 W + | 50 %, filler: solid Phthalate, contains free flowing additive |
| | PEROXAN BP-Powder 50 SE | 50 %, filler: Gypsum |
| | PEROXAN BP-Powder 20 | 20 %, filler: Gypsum |
| Packaging: | Standard packaging of 20 kg resp. 25 kg cardboard box.<br>Small bags, starting from 50 grs. as special packaging on request. | |
| Paste (for Putties): | PEROXAN BP-Paste 50 PF | 50 %, Phthalate free paste |
| Colours: | Red and white colour as standard, other colours (blue and black) on request. | |
| Packaging: | Standard packaging of 25 kg pail.<br>Tubes and cartridges, starting from 5 grs. as special packaging on request. | |
| Speciality: | Customer specified printing (up to three colours) of tubes and cartridges on request | |
| Suspension: | PEROXAN BP-40 LV | 40 %, suspension, phlegmatized |
| | PEROXAN BP-40 W | 40 % (50 %), suspension in water |
| Packaging: | Standard packaging of 25 kg resp. 30 kg container or pail.<br>Supply in IBC possible on request. | |
| Please note: | The suspensions are designed for automatic dosage, i. e. they are suitable for continuous automatic production equipment. | |

The dosage related to resin = 100 % (filler not included) is about 1.0 % to 2.0 % technical pure Dibenzoyl peroxide (= 100 %). Only for resins which contain a high amount of fillers or curing at very low ambient temperatures a higher dosage is recommended.

The following Amine accelerators and formulations are part of our product range:

| Chemical Name | Product Name | Remarks |
|---|---|---|
| N,N-Dimethyl para-toluidine | PERGAQUICK A100 | technical pure liquid |
| N,N-Di-(2-hydroxyethyl) para-toluidine | PERGAQUICK A150<br>PERGAQUICK A15 X | technical pure liquid<br>10 %, solution in TXIB |
| N,N-Dimethyl aniline | PERGAQUICK A200<br>PERGAQUICK A2 X<br>PERGAQUICK A2 S | technical pure liquid<br>10 %, solution in TXIB<br>10 %, solution in Styrene |
| N,N-Diethyl aniline | PERGAQUICK A300<br>PERGAQUICK A3 X<br>PERGAQUICK A3 S | technical pure liquid<br>10 %, solution in TXIB<br>10 %, solution in Styrene |
| Packaging: | Standard packaging of 190 kg resp. 200 kg barrel (PE or metal) or 25 kg resp. 30 kg container (PE or metal). | |

The efficiency of the several Amine accelerators can be obtained from the following table (results obtained from curing of a standard resin (Palatal P6) at 22 °C):

| **Utilized Peroxide:** PEROXAN BP-Powder 50 W, dosage = 3.0 % | **Accelerator Dosage** | **Gel Time [min.]** | **Curing Time [min.]** | **Demoulding Factor (ratio of curing time to gel time)** |
|---|---|---|---|---|
| PERGAQUICK A100 | 0.1 % | 12 | 15 | 1.40 |
| PERGAQUICK A150 | 0.1 % | 14 | 18 | 1.29 |
| PERGAQUICK A200 | 0.1 % | 20 | 24 | 1.20 |
| PERGAQUICK A300 | 0.1 % | 168 | 172 | 1.02 |

The dosage related to resin = 100 % (filler not included) is about 0.1 % to 0.3 %, related to technical pure Amine. It should not fall below the lower limit of 0.1 %, because an under curing may be obtained. Amines do not act as catalyst, they are consumed during reaction. By varying the peroxide dosage, the Amine dosage as well as the type of Amine a broad range for the pot life can be obtained.
Amine pre-accelerated resins can be manufactured after weeks or months, if they are stored in a cool place. While resins containing Dibenzoyl peroxide can still be manufactured for some days.
For all standard applications a combination of a 50 % Dibenzoyl peroxide formulation and PERGAQUICK A200 or PERGAQUICK A150 is recommended. As Amines are classified as toxic materials, we strongly recommend to utilize - if possible - PERGAQUICK A150 - as this Amine is much less toxic.
With respect to other cold curing systems the system Amine accelerator / Dibenzoyl peroxide doesn´t show a reasonable temperature dependence of the curing speed. This is because the dissipated heat of polymerization is always sufficient to increase temperature of the part to be cured above the level of ambient temperature. Therefore this system allows also curing at unfavorable conditions, e.g. winter temperatures. However, without post curing the degree of curing will be not sufficient.
Curing of thick layers may result in stress cracks, due to the spontaneous heat dissipation. Therefore the type of Amine, its dosage and maybe also the peroxide dosage has to be matched accordingly.
Curing of thin layers may result in sticky surfaces, due to the free radical inhibition by the Oxygen of the ambient air. Protection of surfaces by foils or adding of PERGADRY to the resin will avoid these sticky surfaces.
The most important disadvantage of the Amine cold curing system is the yellowing of the final parts, caused by the decomposition products of the Amines. Aging and influence of weathering will cause an additional increase of color intensity, but can be avoided by addition of UV stabilizers.

### Cobalt Accelerated Cold Curing Systems

Cobalt accelerators are solutions of organic Cobalt compounds (complex molecules), like Cobalt Naphthenate or - more common - Cobaltoctoate. These Cobaltoctoate solutions in combination with Ketone peroxides are the so called Cobalt accelerated cold curing system. The cold curing of Ketone peroxide without addition of Cobalt does not work. In the following table you will find the basic curing characteristics of the three different Ketone peroxides, suitable for the cobalt accelerated cold curing.

| | | |
|---|---|---|
| Cyclohexanon peroxides | short gel time | long curing time, without real peak temperature |
| Acetylacetone peroxides | longer gel time | immediate curing, with well-developed peak temperature |
| Methyl Ethyl Ketone (MEKP) peroxides | gel time in the middle of both a.m. peroxides | less immediate curing, less well-developed peak temperature |

All above mentioned Ketone peroxides need the addition of Cobalt. However, with increasing Cobalt dosage the curing characteristic of all Ketone peroxides get closer to each other. At increasing Cobalt dosage the heat dissipation also increases, resulting in higher peak temperatures. The following basic types of Ketone Peroxides are available in our product range.

| Product Name | Remarks |
| --- | --- |
| **Standard products for normal applications:** | |
| PEROXAN ME-50 L/LY/ LX | AO = ca. 9.1 %; normal active MEKP |
| PEROXAN ME 50 LS-PX | AO = ca 9.1 %; super high active MEKP |
| **Standard products for special applications:** | |
| PEROXAN ME-50 LA | AO = 8.9 %; low active MEKP |
| PEROXAN ME-50 LS | AO = 9.7 %; higher active MEKP |
| PEROXAN ME-50 LS-D | AO = 9.7 %; high active MEKP |
| PEROXAN ME-50 LS-P 10 X | AO = 9.7 %; super active MEKP |

Depending on the isomer composition (which is depending on the production process) and the selection of suitable solvents a range of MEKPs with different activities can be formulated.
For all standard applications we offer a normal active - PEROXAN ME-50 L/LY/LX - and a high active MEKP - PEROXAN ME-50 LS-P. Both products offer excellent cost effectiveness.
For special application we also offer a broad range, starting with low active types, like the PEROXAN ME 50 LA, which is recommended for curing of thick layers (avoids stress cracks), up to super active types, like the PEROXAN ME 50 LS-P 10 X. A typical application for this product is the manufacturing of button sheets by casting or rotational moulding. PEROXAN ME-50 LS-P 10 X will give a rapid cure with high exothermic behavior, which is important as a button sheet is only a thin layer. A complete degree of curing will not be reached. Therefore the sheets can be further processed (e.g. punching) without the danger of crack formation. The complete degree of curing is achieved by post curing. In order to maintain the typical curing characteristic of MEKP the Cobalt dosage shouldn`t be lower than 0.5 % of a 1 % Cobalt solution.

| Product Name | Remarks |
| --- | --- |
| PEROXAN C-50 L | AO = 5.4 %; normal active type |

A general advantage of Cobalt accelerated cold curing systems with respect to Amine accelerated systems is that they face no change in colour over time as well as a no change in colour during weathering of the final parts. Especially Cyclohexanone peroxides will show these outstanding properties, if Cobalt dosage is as low as possible.
Due to the curing characteristic of Cyclohexanone peroxide - fast gelation and slow curing - it is highly recommended for the even, tension free curing of lacquer layers and high quality final parts. Due to the fast gelation, the final parts can be further processed after a very short time. This can happen without the risk crack formation in consequence of the further processing steps, as - due to the slow curing – the parts will take some time until they have reached their final hardness.

| Product Name | Remarks |
| --- | --- |
| PEROXAN A-40 L | AO = 4.1 % |

Due to its very fast curing, PEROXAN A-40 L is highly recommended for all applications, which require short demoulding times. Also for heat supported continuous applications it is recommended, as it results in higher production capacities / lower cycle times than MEKP.
The system PEROXAN A-40 L with high addition of Cobaltoctoate, resp. Cobaltoctoate / Amine mix accelerator is also suitable for curing at very low ambient temperatures - nearly similar to the system Amine accelerator / Dibenzoyl peroxide. In order to maintain the typical curing properties of PEROXAN A-40 L a minimum dosage of 1.0 % of a 1.0 % Cobalt solution is required.
Due to the high peak temperature pure Acetylacetone peroxide is not suitable for curing of thick layers (stress cracks).
The curing characteristics of some selected Ketone Peroxides depending on the Cobalt accelerator dosage are listed in the table below. Curing is performed utilizing a standard resin (Palatal P6 at 22 °C).

Please note:
In general it has to be underlined, that the results of curing experiments obtained with a standard resin cannot be transferred without restrictions to any other resin. Fillers as well as other resin additives may lead to deviations.

| Ketone Peroxide (dosage of supplied form = 2.0 %) | Cobalt Accelerator Dosage (1 % solution) | Gel Time [min.] | Curing Time [min.] | Demoulding Factor |
|---|---|---|---|---|
| PEROXAN A-40 L | 0.2<br>0.5<br>1.0 | 42<br>12<br>7 | 50<br>16<br>10 | 1.19<br>1.33<br>1.43 |
| PEROXAN C-50 L | 0.2<br>0.5<br>1.0 | 28<br>9<br>5 | 37<br>17<br>12 | 1.32<br>1.89<br>2.40 |
| PEROXAN ME-50 L/LY/LX | 0.2<br>0.5<br>1.0 | 40<br>15<br>7 | 50<br>23<br>14 | 1.25<br>1.53<br>2.00 |
| PEROXAN ME-50 LS-P | 0.2<br>0.5<br>1.0 | 20<br>9<br>4 | 30<br>16<br>10 | 1.50<br>1.78<br>2.50 |

The demoulding factor, i.e. the ratio from gel time to curing time isn`t very reasonable for Cobalt accelerated curing systems, especially not at high Cobalt dosages.

### Ketone Peroxide Mixtures:

For certain applications the curing characteristics of pure Ketone peroxides are not sufficient. In order to offer an appropriate hardener we supply a broad range of peroxide mixtures. In addition we also offer to develop and produce new tailor-made mixtures for our customer`s requirement. Some examples of existing mixtures are listed in the following tables:

| Product Name | Remarks |
|---|---|
| PEROXAN A-50 M | AO = 5.20 % |

PEROXAN A-50 M is blended in a way, that it corresponds exactly to PEROXAN ME 50 L/LY/LX with respect to gel time and peak temperature, but it allows shorter demoulding times.

| Product Name | Remarks |
|---|---|
| PEROXAN M-64 AX | AO = 7.9 % |

Compared with PEROXAN ME 50 L, utilization of PEROXAN M-64 AX will result in a little longer gel time, but shorter curing and demoulding time, making it an ideal curing system with good advantages for many applications.

| Product Name | Remarks |
|---|---|
| PEROXAN C-50 LM | AO = 9.7 % |

Addition of MEKP to Cyclohexanone peroxide will result in a faster cure with higher peak temperature with respect to pure Cyclohexanone peroxide, but maintaining the same short gel time.

<u>Packaging of our Ketone peroxides:</u>
All above mentioned Ketone peroxides / formulations are available - besides the standard packaging of 25 kg / 30 kg containers - in various packaging (down to bottles with 50 grs. content) on request. Dyeing in red is also possible on request.

<u>Dosage of our Ketone peroxides:</u>
The dosage related to resin = 100 % (without fillers) is 1 % up to 3 %, related to the supplied formulations.

### Cobaltoctoate:

The following Cobaltoctoate solutions are available in our product range:

| Product Name | Remarks |
|---|---|
| PERGAQUICK C100 | 10 %, solution in Xylene |
| PERGAQUICK C60 X | 6 %, solution in TXIB |
| PERGAQUICK C12 X | 1 %, solution in TXIB |
| PERGAQUICK C11 | 1 %, solution in Styrene |
| PERGAQUICK C24 AX | Cobaltoctoate/Amine (DMA) mix, solution in TXIB |
| Packaging: | Standard packaging of 190 kg resp. 200 kg barrel (PE or metal) or 25 kg resp. 30 kg container (PE or metal). |

Cobalt / Amine accelerators are suitable for curing at low ambient temperatures. The Amine is acting as a promoter, generating the required heat necessary to start the accelerating activities of Cobalt on the peroxide.
Contrary to Amines, Cobaltoctoate is acting as a catalyst and a minimum dosage level doesn`t exist. Common are 1 % solutions, like PERGAQUICK C 12 or C 11, due to the more exact dosage. Regarding PERGAQUICK C 11 (solvent = Styrene) one should be aware of the limited storage life! The dosage related to resin = 100 % is about 0,1 % to 3,0 % related to 1 % Cobaltoctoate solutions. For curing of lacquer films the dosage can be up to 6 %, as Cobalt acts also as siccative (drying agent).
Cobalt accelerated resins can be processed after months, if stored at a cool place. Fillers may reduce the Cobalt accelerating effect, due to physical absorption. Ketone peroxide containing resins will start gelation after several hours. Inhibitors will not sufficiently enlarge the pot life of these mixtures. More efficient is also a storage at low temperatures (refrigerator).

### Cold Curing of Vinylester Resins

As a general guideline: Do not try to transfer the rules valid for curing of UP resins to Vinylester resins! All is the opposite way around!
Ketone peroxides, which yield a slow curing with UP resins, will show a fast curing with Vinylester resins. Solvents acting as promoter in UP resins, act as inhibitor when used in Vinylester resin curing. Besides one exception, only Cobalt / Amine mix accelerators are effective.
Another characteristic of Vinylester resins will be that all mixtures with peroxides containing Hydrogene peroxide ($H_2O_2$) have a more or less foaming tendency. However, if the foaming stops within the potlife of the activated resin, this problem is of minor importance.
Peroxide formulations, based on Cumene hydroperoxide, do not show any foaming. We recommend the following products of our product range for curing of Vinylester resins. Other tailor made products are available on request:

| Product Name | Remarks |
|---|---|
| PEROXAN C-50 L | Cyclohexanone peroxide, AO = 5.4 %<br>fast curing, evtl. Foaming |
| PEROXAN ME-50 LA | Methyl Ethyl Ketone peroxide, AO = 8.9 %<br>fast curing, very low tendency of foaming |
| PEROXAN CU-80 L | Cumene hydroperoxide, AO = 8.4 %,<br>solution in Cumene, a little slower curing,<br>better degree of curing, no foaming |
| PEROXAN CU-40 M | Cumene hydroperoxide, AO = 4.2 %,<br>solution in Ethylacetoacetate,<br>curing / degree of curing like<br>PEROXAN CU 80 L, no foaming,<br>Cobalt / Amine mix accelerator not required,<br>Cobalt accelerator is sufficient |

### Hot Curing Systems

The hot curing, i.e. the curing without addition of accelerator, requires heat supply. The advantages of hot curing are:

- very fast curing at high degree of curing
- a long pot life of the activated resin

Hot curing processes are utilized especially for automatic processing, where expensive machineries require a high production capacity / short cycle times. Hot curing processes are hot pressing, processing of SMC / BMC, pultrusion, continuous impregnating of sheets, injection moulding, RTM and relining (repair of damaged concrete waste water tubes).
Temperatures of approx. 80 °C (typical temperatures are 120 °C to 160 °C) are required to start peroxide decomposition and to achieve a sufficient degree of curing within a short time. The shorter the required curing time (e.g. for hot pressing between 1 and 5 min.), the higher must be the curing temperature. If for technical reasons a certain temperature level cannot be increased, a peroxide with a lower activating temperature must be selected.
For a cost effective use of the machinery it is necessary to prepare larger lots of activated resin. This requires a pot life of several days for the activated resin. For resin mixtures with a peroxide of higher activating temperature this will not be a problem. If necessary the activated resin has to be stored at a cool place. However, if peroxides are utilized in combination with Cobalt accelerators (several hot curing peroxides can be accelerated by addition of Cobalt), the activated resin will only have a pot life of some hours.
In many applications combinations of two or three different peroxides are used. This happens either in form of a ready to use peroxide mixture or they are added separately. The most active peroxide of this combination has to start polymerization and generate sufficient heat for starting the decomposition of the peroxides with a lower activity. A well selected and tuned peroxide combination is highly effective, ensuring a smooth curing and an excellent degree of curing. The following peroxides and peroxide formulations, suitable for hot curing, are part of our product range:

| Product Name | Chemical Name | Activat. Temp. | Remarks |
|---|---|---|---|
| PEROXAN BCC | Di-(4-tert.-butyl cyclohexyl)-peroxydicarbonate | 60 °C | temperature controlled product, storage at max. + 15 °C, technical pure powder |
| PEROXAN BCC 40-W | | | 40 %, water based suspension |
| PEROXAN MI-60 KX | Methyl Isobutyl Ketone peroxide | 70 °C - 85 °C | activation temp. depends on the Cobalt dosage, but adding Cobalt will also result in a short pot life |
| PEROXAN MI-60 KPX | Peroxide mixture | | mixture of MIKP and tert.-Butyl-peroxy benzoate, liquid, ready-to-use mixture |
| PEROXAN LP | Dilauroyl peroxide | 80 °C | technical pure powder or flakes |
| PEROXAN BP .... | Dibenzoyl peroxide | 90 °C - 95 °C | available formulations see product brochure |
| PEROXAN PO | tert.-Butylperoxy 2-ethylhexanoate | 90 °C - 95 °C | temperature controlled product, storage at max. + 15 °C, technical pure liquid |
| PEROXAN PO-50 P | | | 50 %, powder with chalk |
| PEROXAN PK295 V-75 | 1,1-Di-(tert.-butyl-peroxy) 3,3,5-trimethyl-cyclohexane | 115 °C | 75 %, solution in Isododecane |
| PEROXAN PK295 V | | | 50 %, solution in Isododecane |

| | | | |
|---|---|---|---|
| PEROXAN PK295 P | | | 40 %, powder with chalk |
| PEROXAN PK122 V | 1,1-Di-(tert.-butyl-peroxy) cyclohexane | 120 °C | 50 %, solution in Isododecane |

| | | | |
|---|---|---|---|
| PEROXAN PIN | tert.-Butylperoxy 3,3,5-trimethylhexanoate | 120 °C | technical pure liquid |
| PEROXAN PIN S1 | Solution in promotor | | 90 %, activated |
| PEROXAN BIC | tert.-Butylperoxy isopropyl carbonate | 120 °C | 75 %, solution in Isododecane |
| PEROXAN BEC | tert.-Butylperoxy 2-ethylhexyl carbonate | 125 °C | Technical pure liquid |
| PEROXAN PB | tert.-Butylperoxy benzoate | 125 °C | technical pure liquid |
| PEROXAN PB-75 | | | 75 %, solution in Isododecane |
| PEROXAN PB-50 P | | | 50 %, powder with chalk |
| PEROXAN DC | Dicumyl peroxide | 135 °C | technical pure granules (sugar like) |
| PEROXAN DC-40 P | | | 40 %, powder with chalk |
| PEROXAN BIB-1 | Di-(2-tert.-butylperoxy) isopropylbenzene | 140 °C | technical pure powder or flakes |
| PEROXAN BIB-40 P | | | 40 %, powder with chalk |
| PEROXAN BU | tert.-Butylcumyl peroxide | 140 °C | technical pure liquid |
| PEROXAN HX | 2,5-Dimethyl-2,5-di-(tert.-butylperoxy-hexane) | 145 °C | technical pure liquid |
| PEROXAN HX-45 P | | | 45 %, powder with chalk |

Peroxides with high activation temperatures (> 130 °C), like PEROXAN DC, PEROXAN BIB, PEROXAN BU and PEROXAN HX are used for hot curing of SMC / BMC at very high curing temperatures.Typical hot curing peroxides for the medium temperature range of SMC / BMC, hot pressing, RTM and injection moulding are the Perketales PEROXAN PK295 ... and PEROXAN PK122 ..., PEROXAN PIN and PEROXAN PB.

For all applications which require a very low residual amount of styrene, PEROXAN BEC is recommended. PEROXAN BEC is equivalent in its curing characteristics to PEROXAN PB and one can easily replace it in the recipes. The achievable residual styrene content by utilization of PEROXAN BEC can be times 100 to 1000 lower. Same applies for PEROXAN BIC, but PEROXAN BIC is a little more active than PEROXAN BEC. Also the Perketales PEROXAN PK122 ... and PEROXAN PK295 ... will lead to reasonable low residual Styrene contents. For the continuous production of sheets and profiles peroxides like PEROXAN MI-60 KX, PEROXAN PO, PEROXAN PK295 ..., PEROXAN PK122 ... and PEROXAN PIN are often used. Either a single peroxide or a combination of peroxides is utilized. We offer, based on Methyl Isobutyl Ketone peroxide, a range of ready-to-use mixtures consisting of two peroxides.Combinations of peroxides, where the most active peroxide generates the heat for the decomposition of the peroxides with higher activation temperatures are used for example in pultrusion or relining. Nearly all of these combinations (consisting of 2 or 3 different peroxides) will start with PEROXAN BCC as the most active peroxide.

A peroxide of medium activity (PEROXAN LP, PEROXAN BP... or PEROXAN PO) and / or lower activity (PEROXAN PK295..., PEROXAN PK122..., PEROXAN PIN or PEROXAN PB) will follow. All combinations are in principle possible. Similar to the activity of PEROXAN BCC will be a mixture of PEROXAN MI-60 KX and Cobalt at high dosage levels. But the pot life of this mixture is extremely short. However, also the pot life of PEROXAN BCC activated resins are not too long at room temperature; it is therefore recommended to keep them at a cool place.

## Inhibitors

Inhibitors are chemical compounds, which prevent polymerization process of monomers or other reactive compounds. Suitable compounds are Quinones or Phenolic compounds, which are able to liberate weak Hydrogen atoms. These Hydrogen atoms react with free radicals from peroxide decomposition or with a growing polymer chain and inhibit any further reaction. This inhibition reaction will end, after all inhibitor molecules are consumed. Inhibitors are therefore not only suitable for enlarging the potlife of activated resins, but also to increase storage life of pre-accelerated resins. The following inhibitors are part of our product range:

| Chemical Name | Product Name | Remarks |
|---|---|---|
| 4-tert.-Butyl catechol | | Increases pot life of activated resins for cold curing applications, without influencing the curing time. Only effective at room temperature. |
| | PERGASLOW BK-100 | technical pure solid,<br>dosage: 0.005 % - 0.05 % (resin = 100 %) |
| | PERGASLOW BK-10 X | 10 %, solution in TXIB |
| 2,6-Di-tert.-butyl para-cresole | | Increases pot life of activated resins, without major influence on the curing time. Also effective at slightly increased temperatures. Highly recommended for stabilizing preaccelerated resins. |
| | PERGASLOW PK-100 | technical pure solid,<br>dosage = 0.04 % - 0.12 % (resin = 100 %) |
| | PERGASLOW PK-40 | 40 %, solution in Xylene |
| | PERGASLOW PK-30 S | 30 %, solution in Styrene |
| Hydroquinone | | Increases storage stability of SMC / BMC |
| | PERGASLOW HD-100 | technical pure solid,<br>dosage: 0.01 % - 0.03 % (resin = 100 %) |
| | PERGASLOW HD-10 | 10 %, solution in Cyclohexanone |

### Disclaimer

The information presented herein is true and accurate and to the best of our knowledge, but without any guarantee. Since the conditions of use are beyond our control we disclaim any liability, including for patent infringement, incurred in connection with the use of these products, data or suggestions.

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